Nonclassical radiation from diamond nanocrystals

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Abstract

The quantum properties of the fluorescence light emitted by diamond nanocrystals containing a single nitrogen-vacancy (NV) colored center is investigated. We have observed photon antibunching with very low background light. This system is therefore a very good candidate for the production of single photon on demand. In addition, we have measured larger NV center lifetime in nanocrystals than in the bulk, in good agreement with a simple quantum electrodynamical model.

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Light sources able to emit individual photons on demand would be of great potential use for quantum cryptography [1,2], A quantum computation scheme requiring such sources has also been proposed recently [3]. Considerable activity is thus dedicated to designing and implementating efficient, robust, room-temperature sources delivering a periodic train of pulses containing one and only one photon. These sources are based on the property of a single emitting dipole to emit only one photon at a time. When excited by a short and intense pulse, such an emitter delivers one and only one photon [4,5]. After pioneering experiments demonstrating photon antibunching [6–8] and conditional preparation of single-photon states [9,10], followed by first attempts to build triggered single photon sources [4,11,12], the present generation of experiments is concentrating on solid-state schemes better suited for practical use, such as single organic molecules [13–16], self-assembled semiconductor quantum dots [17,18], or semiconductor nanocrystals [19]. The succesful candidate should work at room temperature, and be photostable.

A promising system for a robust single photon source is provided by individual nitrogen-vacancy (NV) color centers in diamond [20], which already permitted to observe photon antibunching under continuous excitation conditions in bulk crystals [21–23]. These color centers have the great advantage of being photostable and do not exhibit any photoblinking. The set-up in these experiments is particularly simple, since it involves diamond samples at room temperature, and non-resonant excitation from a laser at 532 nm, with a typical power in the mW range. However, a significant limitation in bulk diamond is that the light is emitted in a high-index material ($n_d = 2.4$), which makes its efficient extraction difficult. Refraction at the sample interface leads to a small collection solid angle and to aberrations. This problem is somehow similar to that encountered in semiconductor light-emitting devices [24].

In this paper, we show that diamond nanocrystals (typical size 50 nm) containing a single NV center offers a very efficient solution to circumvent these problems [25]. The subwavelength size of these nanocrystals renders refraction irrelevant. One can simply think of the nanocrystal as a point source emitting light in air. Furthermore, the small volume of diamond excited by the pump light yields extremely small background light. This is of crucial importance for single photon sources, since background light contributes to a non-vanishing probability of having two or more photons within the light pulse.

In addition, the width of the dip of the fluorescence intensity autocorrelation function $g^{(2)}(t)$ gives information about the lifetime of the emitters. Using this technique, we have observed an increase of the lifetime of a NV center in a nanocrystal compared to the bulk value [26]. This effect arises from the fact that, in a nanocrystal, the center can be considered as radiating in air, whereas it radiates in a medium of index of refraction $n_d = 2.4$ in bulk [27]. Our results tend to suggest that the local field experienced by the NV center is the same in the bulk and in a nanocrystal, and are therefore independent of local field corrections, which have been a controversial issue during the last decade [28–30].

The color center used in our experiments is the NV defect center in synthetic diamond, with a zero phonon line at a wavelength of 637nm [20]. The defect consists in a substitutionnal nitrogen and a vacancy in a adjacent site. A simplified level structure is a four-level scheme with fast non radiative decays within the two upper states and within the two lower states. The excited state lifetime in the bulk is $\tau_b = 11.6$ ns [31]. The nanocrystals come from synthetic diamond powder bought from de Beers. The defects are created by irradia-

tion with 1.5 MeV electrons at a dose of $3 \times 10^{17} e^-/\text{cm}^2$, and annealing in vacuum at 850^{o}C during 2 hours. The density of NV centers created is then estimated to be of one in a 30 nm diameter sphere [20]. The nanocrystals are dispersed by sonification in a solution of polymer (Polyvinylpyrrolidone at 1 weight% in propanol). This allows the disaggregation of the particles and their stabilisation in a colloidal state. Centrifugation at 11000 rpm for 30 mn allows us to select nanocrystal sizes of $d_0 = 90 \pm 30$ nm (measured by dynamical light scattering). The average number of NV centers in a nanocrystal has been evaluated to 8 (see below). Nanocrystals containing a single NV center should therefore have a size around $d_0/2 = 45$ nm, which lies in the lower wing of the size distribution. The nanocrystal solution is then spin coated at 3000 rpm on thin fused silica substrates. Evaporation of the solvent leaves a 30 nm thick film of polymer with the nanocrystals well dispersed on the surface. Their density was estimated to be around 0.02 μm^2. In most experiments we look at the centers from the other side of the plate, which is in contact with the oil of an immersion microscope lens (Nachet 004279, N.A. = 1.3).

The experimental set-up has been described in detail elsewhere [22]. It is based upon a home-made scanning confocal microscope, where the sample is excited using continuous-wave frequency-doubled YAG laser ($\lambda = 532$ nm). The fluorescence light (wavelength between 637 and 800 nm) is collected by the same objective and separated from the excitation laser by a dichroic mirror and filters. It can be sent either to a spectrometer, or to a standard intensity correlation set-up using two avalanche photodiodes (EG&G, model SPCM-AQR 13), a time to amplitude converter (TAC) and a computer data acquisition board. The time bin is 1 ns, and a delay of 50 ns in one TAC input allows us to get data for negative time. A slow (8 s response time) x-y-z computerized servo-lock is used to maintain the fluorescence on its maximum for the observed center.

It is worth pointing out that the remarkable photostability of NV centers in bulk [20–22] is preserved in nanocrystals. Fluorescence has been observed in the saturation regime for hours without any photobleaching nor blinking.

Fig. 1(a) displays a 2D scan of nanocrystal containing a single NV center. The resolution of 500 nm is that of the confocal microscope. The line scan in Fig. 1(b) shows that the signal (S) to background (B) ratio is very good with a value $S/B = 20$. Note that B is the count rate measured about 2 μm away from a nanograin.

Fig. 2 shows the fluorescence rate of a NV center in a nanocrystal and in bulk diamond as a function of the pump power. Slightly decreasing rate for high pump power is attributed to the presence of an additionnal shelving state. It can be seen that the contribution of the background is greatly reduced in the nanocrystal configuration. The count rate in the nanocrystal is not as high as expected. However a fair comparison with the bulk should take into account the $\tau_{nc}/\tau_b = 2.2$ factor increase of the NV center lifetime in a nanocrystal (see below). The number of photons emitted in a lifetime is then larger in the nanocrystal.

The raw coincidences $c(t)$ (right axis) and autocorrelation function $g^{(2)}(\tau) = \langle I(t)I(t+\tau)\rangle/\langle I(t)\rangle^2$ (left axis) are represented in Fig. 3. For evaluating the intensity correlation function $g^{(2)}(t)$ of the NV center, the raw correlation data $c(t)$ is normalized and corrected in the following way. The raw coincidence rate $c(t)$ counted during a time T within a time bin of width w is first normalized to that of a Poissonian source according to the formula $C_N(\tau) = c(\tau)/(N_1 N_2 w T)$, where $N_{1,2}$ are the count rates on each detector. Then the normalized coincidence rate $C_N(\tau)$ is corrected for the background light, and we obtain

$g_c^{(2)}(\tau) = [C_N(\tau) - (1-\rho^2)]/\rho^2$, where $\rho = S/(S+B)$ is the signal to background ratio, which is measured independently in each experimental run. Note that we have checked experimentally that the background light has a Poissonian statistics. It can be seen in Fig. 3 that $g^{(2)}(0) \sim 0$, where the slight difference with zero is attributed to remaining background light emitted by the nanograin. This almost vanishing value of $g^{(2)}(0)$ is the signature of the presence of a single emitter in the observed nanocrystal. In the case of the presence of p centers within an unresolved peak, the value of the zero-time antibunching is $1 - 1/p$. This is actually how we estimate the number of NV centers in a nanocrystal. It should also be mentionned that $g^{(2)}(\tau)$ reaches values greater than unity for $\tau \neq 0$. This bunching effect is due to the presence of a third state in which the system can be shelved [23,32].

Obviously, for the ultimate achievement of a true single photon source, no background subtraction is possible and the meaningful quantity is the experimentally measured $C_N(0)$. Indeed, when the center is excited by a short an intense pulse, the probability p_2 of having more than 2 photon in a pulse is given by (assuming $p_2 \ll 1$)

$$p_2 = C_N(0)\, p_1^2/2 \tag{1}$$

where p_1 is the probability of having a single photon. Note that for Poissonian light $C_N(0) = 1$ and eq.(1) gives the photon probability distribution of an attenuated coherent pulse. In our case $C_N(0) = 0.17$ at the fluorescence rate maximum (input power of 2.7 mW), where the best value in bulk was 0.26 [21,23]. This would yield to significant improvement compared to attenuated coherent pulses which are usually used in quantum cryptography experiments [1].

The central dip in the antibunching traces can be fitted by an exponential function of argument $-(k_{12}+k_{21})\,|\tau\,|$, where k_{12} and k_{21} are respectively the pumping rate and the NV center lifetime. Such fits have been performed for different pumping powers. The lifetime $k_{21} = 1/\tau_{nc}$ of an NV center in a nanocrystal can then be inferred by extrapolating the value of the time constant for vanishing pump power. Fig. 4 shows a lifetime of $\tau_{nc} = 25$ ns for the observed NV center. By looking at 10 different nanocrystals we have found a lifetime of 25 ± 4 ns, where the lifetime of a NV center in synthetic bulk diamond is $\tau_b = 11.6 \pm 0.1$ ns [31]. This dispersion may be attributed to the dispersion in nanocrystal size. When going from bulk diamond to nanocrystals, the refractive index of the surrounding medium is strongly modified. This leads to a change of the lifetime of the center. In a simple approach, the squared amplitude of the one-photon electric field should be divided by the relative susceptibility $\epsilon_r = n^2$, while the mode density, which is proportional to the elementary volume in the wavevector space, should be multiplied by n^3. Since the lifetime is proportional to the product of these two quantities, one obtains the simple formula [27]:

$$\Gamma_n = n\Gamma_v \tag{2}$$

relating the spontaneous emission rates Γ_n in the material and Γ_v in the vacuum. In our case, the NV center in bulk diamond emits within an medium of index $n_d = 2.4$, and the center in a sub-wavelength nanocrystals emits in air for one half of the space, and in fused silica (refractive index $n_s = 1.45$) for the other half. The expected value from eq.(2) is then $\tau_{nc} = \tau_b[2n_d/(1+n_s)] = 22.7$ ns in good agreement with the experimental values.

In the case of modification of the immediate surroundings of the emitting dipole, eq. (2) becomes $\Gamma_n = nl^2\Gamma_v$, where l is the local field enhancement factor. Different models lead to different local field correction factors, and this topic is actively discussed in the literature [28–30]. However our experimental results agree well with eq. (2). This supports the statement that the local field experienced by the NV center is the same in the bulk and in a nanocrystal. Indeed the immediate environment of the NV center at a scale of $\sim 1nm$ (ie a few crystalline periods) is unchanged. It is thus worth pointing out that in our case, local field corrections are not needed, and that the simple quantum electrodynamical analysis of eq. (2) is valid.

As a conclusion, we have observed almost background-free photon antibunching from single NV centers in diamond nanocrystals at room temperature. The photostability of NV centers in bulk diamond is preserved, allowing us to lock the laser beam on a single center during several hours. Manipulation of nanocrystals is a lot more flexible than bulk crystals. Straightforward improvement of the light collection efficiency should be possible by letting the nanocrystal sit on a metallic mirror, or inserting it in a microcavity [33–35]. These results show that diamond nanocrystals offer all the required properties for the realization of efficient single photon sources for quantum information systems. In addition, we found conclusive evidence that the lifetime of a NV center is larger in nanocrystals than in bulk owing to change of the surrounding index of refraction.

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FIGURES

FIG. 1. (a) Confocal microscopy raster scan ($5 \times 5\ \mu\mathrm{m}^2$) of a diamond nanocrystal containing a single NV center. The size of a pixel is 100 nm and the integration time per pixel is 32 ms. The laser intensity impinging on the sample is 2.7 mW. In (b) is displayed a linescan along the dotted line of (a), together with a gaussian fit, which is used to evaluate the signal and background levels. Here we obtain $\rho = S/B = 20$.

FIG. 2. Fluorescence rate of a NV center in a nanocrystal (a) and in bulk diamond (b) as a function of the pump power. The "+", "□", "•" represent respectively the background B, the total count rate $T = S + B$, and the signal from the center $S = T - B$. The maximum number of photons emitted in a lifetime is 5.5×10^{-4} for the nanocrystal (lifetime $\tau_{nc} = 25$ ns) and 3.7×10^{-4} in the bulk (lifetime $\tau_{nc} = 11.6$ ns). The data for the nanocrystal corresponds to the center of Fig. 1.

FIG. 3. Autocorrelation function $g^{(2)}(t)$ (left) and raw coincidence rate (right). The time bin $w = 0.3$ ns. The total integration time is 323 s. The laser intensity impinging on the sample is 2.7 mW. The actual number of coincidences is indicated on the right. The zero-time value of the uncorrected normalized correlation function is $C_N(0) = 0.17$. The fit is performed with the model used in [23]. The data corresponds to the center of Fig. 1.

FIG. 4. Width of the exponential dip of antibunching traces obtained at different pump power. The extrapolation for vanishing pump power gives the lifetime. The "•" correspond to the data of Fig. 1 and yield $\tau_{nc} = 25$ ns. The "□" correspond to a NV center in bulk diamond ($\tau_b = 11.6$ ns). The slope in the nanocrystal is twice as large as that in bulk which is consistent with the lifetime increase, since the NV center in a nanocrystal can absorb twice as many photons during its lifetime.